EVAPORATION OF FREELY SUSPENDED AND CHARGED WATER DROPLETS

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ABSTRACT. Experimental data for the evaporation of water droplets of 1μ size, evaporating in humid air, are obtained These droplets are charged and are freely suspended in air. After adequate correction for the cooling of droplets due to evaporation, $r\ dr/dt$ is found to be proportional to $\{\rho_v(s)-\rho_v\}$, over a considerable range However, at very low values of $\{\rho_v(s)-\rho_v\}$, a departure from such a trend is indicated. In every case, the rate of evaporation for charged droplets of 1μ size, is found to be considerably less than that calculated from Fuchs' theory for uncharged droplets.

INTRODUCTION

The evaporation of organic liquid droplets evaporating in air, has been the subject of extensive experimental observations. The variation of the rate of evaporation with droplet radius, temperature and pressure has been observed. Such evaporation rates have been noted for attached, as well as, unattached droplets of several such liquids.

The evaporation of water droplets in gaseous media and the reverse process of droplet growth by condensation, are extremely important in nature. The cycle of water proceeds via the condensation of water vapor on hygroscopic particles in the troposphere, with the formation of cloud droplets. Such droplets either evaporate, depending on the turbulence and the environmental conditions, or form bigger rain drops. It is also well-known that charge is present in a cloud. Thus the study of evaporation rates of small charged water droplets, under controlled conditions, is extremely important in the relatively new field, cloud physics.

THEORETICAL AND EXPERIMENTAL BACKGROUND

The basis of the theory of evaporation of droplets in gaseous medium was laid by Maxwell. Considering purely diffusion control of evaporation, Maxwell arrived at the following equation, for the rate of decrease of droplet radius

$$\frac{dr}{dt} = -\frac{D}{\rho_L r}\{\rho_v(s)-\rho_v\} \qquad \dots (1)$$

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where, r is the drop radius, D the diffusion coefficient of water vapour in air $\rho_v(s)$, ρ_v are respectively the vapour densities at the surface of the drop and in the distant environment, and ρ_L is the density of liquid water.

But it soon became evident that, when the droplet radius is comparable to the mean free path of a diffusing vapour molecule, Maxwell's expression does not hold good. Fuchs (1934) derived theoretically a more adequate expression for such an evaporation rate, which is given by

$$\frac{dr}{dt} = -\frac{\alpha\nu}{\rho_L\left(1+\frac{\alpha\nu r}{D}\right)}\{\rho_v(s)-\rho_v\} \quad \dots \quad (2)$$

where α is the condensation coefficient and $\nu = (kT/2\pi m)^{\frac{1}{2}}$ in the usual notation.

Frisch and Collins (1952) derived the same expression as that of Fuchs by more analytical methods based on stochastics. Monchick and Reiss (1954), on the other hand, have developed a theoretical formalism using non-Maxwellian distribution functions They have concluded that, except for small modifications in the constants, Fuchs expression is correct to the first order in their perterbation theory.

Woodland and Mack (1933), Shereshefsky and Steckler (1936), Bradley, Evans and Whytlaw-Gray (1946), Birks and Bradley (1949) as well as Monchick and Reiss (1954) have experimentally observed the evaporation rates for droplets of organic liquids under different conditions of pressure and temperature. They have all confirmed Fuchs expression for the evaporation rates of such droplets of organic liquids, evaporating in dry air.

Gudris and Kulikova (1924) measured the rate of evaporation of charged water droplets, with an aqueous solution in the chamber, with vapor pressure 2.5mm (i.e., approx. 15%) lower than that of the saturated vapour. In this case, initial radius decreased steadily for 40 minutes from 0.64 to 0.49μ. This rate was many times less than the theoretical. It was thought desirable therefore, to check the evaporation rates for 1μ size water drops which are freely suspended and charged, under more exact conditions of pressure, temperature and relative humidity, inside a chamber.

EXPERIMENTAL TECHNIQUE AND PROCEDURE

The Millikan's oil-drop apparatus of 'CENCO' design has been used for the observation of water droplets in the present experimental investigation. The plate separation was adjustable to either 0.53cm or 0.7 cm. The 400V D.C supply required for these observations, was obtained by connecting nine 45V batteries in series. The illumination of the droplets was provided by converging a beam of light. Adequate precautions were taken to avoid any significant drift of the droplet due to uneven heating. The smallest division of the tele-microscope, used for observing the droplet transit, measured 0.081 cm.

To measure accurately the relative humidity of the air, inside the small chamber of Millikan's apparatus, a special form of the dew-point hygrometer was developed. In this apparatus, the dew was formed on the end of a narrow silver tube, inserted inside the chamber, by cooling the tube with the help of a controlled flow through it of pre-cooled ethyl ether. The temperature of the surface, where dew is formed, was noted accurately with the help of a thermo-couple. Only a small portion of the tube was exposed, as the rest was covered by rubber tubing. This hygrometer allowed the determination of relative humidity within the small chamber, quite accurately as described by N.R. Gokhale and K. M. Gatha (1959).

In the present series of experiments a set of observations was charactarised by some constant values for pressure, temperature and relative humidity. The same selected droplet freely suspended between the two plates was repeatedly observed in such a set of observations. This was accomplished by bringing the droplet which was charged due to friction while spraying, to its original position everytime, by applying the electric field. In this manner, the free fall under gravity was observed for the same droplet at various epochal times 't'. At every epochal time 't' the time t_g for the free fall of the droplet through one division of the tele-microscope was noted. The time tg was small as compared to the time interval between two successive epochs. The velocity V_g, of free fall under gravity was thus obtained from t_g, for each value of t. Next, for each 't' the droplet radius r was calculated with the help of the equation

$$r = \left\{ \frac{9\eta V_g}{2g(\rho - \rho_a)} \right\}^{\frac{1}{2}} \qquad (3)$$

where $\eta = 183.2 \times 10^{-6}$ dynes per sq. cm, is the coefficient of viscosity for air, $\rho_L = 0.996$ gm cm^{-3} is the density of water, $\rho_a = 0.00129$ gm cm^{-3} is the density of air, while g is the acceleration due to gravity.

The above expression for r in terms of Vg is based upon Stokes' law. However, it is known that this law needs correction when the droplet-radius is comparable to the mean free path of air molecules. According to Millikan (1923), the corrected value of Vg is

$$V_g^1 = V_g \left(1 + A\frac{l}{r}\right)^{-1} \qquad \ldots \quad (4)$$

where $l = 9.6 \times 10^{-6}$ cm, is the mean free path for air molecules at room temperature and atmospheric pressure, while A is the correction constant to be determined empirically. Millikan has shown that A depends upon the droplet-liquid and the medium through which the droplet falls.

To determine the constant A, which is not known, for water droplets falling through air, a special experiment was performed. The procedure was similar to that used by Millikan. However, the evaporation rate for water droplets in air is rather large. Hence, special precautions were necessary to prevent any significant change in the droplet radius during the time of each observation. This was accomplished by reducing the time of observation and by saturating the air by placing water-boats inside the chamber. This experiment, gives $A = 0.701$ for water droplets falling through air, as described by N. R. Gokhale and K. M. Gatha (1958).

By inserting the corrected velocity Vg' into Eqn. (3), the corrected droplet radius was calculated for each value of 't' The evaporation rate dr/dt was next calculated from the above set of values of r and t.

RESULTS

The evaporation rate for water droplets, evaporating in humid air, is expected to depend upon pressure, temperature, the droplet radius and the relative humidity of air All observations reported herein have been carried out at atmospheric pressure equal to 76 cm of Hg and temperature 28°C approximately. The present series of experiments consist of over seventy sets of observations.

The principal purpose of the present investigation has been to observe the dependence of the evaporation rate on relative humidity. Thus, these sets of observations correspond to the droplet radius equal to $(10 \pm 2) \times 10^{-5}$ cm, while the temperature was kept at 28°C approximately. On the other hand, the relative humidity was systematically varied from 0.20 to 0.85. The corrected droplet radius was plotted against t for each set of observations It was found that the experimental points fell on a straight line for each such set of observations with relative humidity greater than 0.3 The evaporation rate (dr/dt) was calculated, for each such set, from the slope of the corresponding straight line. Four such sample plots are shown in Fig. 1 On the other hand, the experimental plots indicated small curvatures for those sets of observations, where the relative humidity was less than 0.3. Four such sample plots are illustrated in Fig. 2. The evaporation rate (dr/dt), in such cases, was calculated from the slope of the tangent to the curve at some value of r, lying within the above range.

Further eight sets of observations at room temperature were taken with the droplet radius varying from 5×10^{-5} cm to 17×10^{-5} cm The experimental values of r plotted against t, in each case, fall on a curve The evaporation rate was next calculated at the two end points of the curve for each set. It was found that in every case the evaporation rate increased with the decrease in the droplet radius as expected from Maxwell's and Fuchs' equations. However, the relative humidity being different for different sets, significantly affected the evaporation rates.

A plot of rdr/dt against $\{\rho_v(s) - \rho_v\}$ failed to produce a linear relationship if $\rho_v(s)$ is assumed to be the saturation vapour density at the temperature of the environment. It was noted however, that a correction for the fall in temperature of the droplet caused by evaporation, was necessary. Kinzer and Gunn (1951)

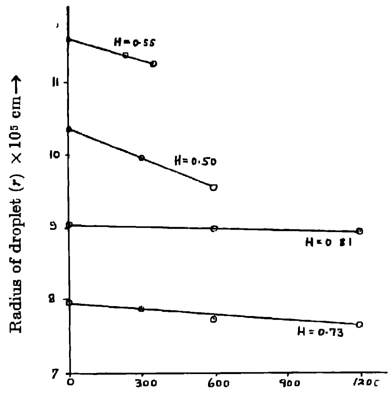

Fig. 1. Variation of radius of droplet with time

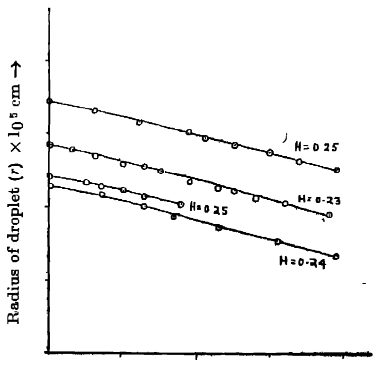

Fig. 2. Variation of radius of droplet with time

determined the temperature of freely-falling drops and showed that this temperature and that of a ventilated wet-bulb thermometer are very close. Hence, $\rho_v(s)$ was assumed to be the saturation vapour density appropriate to the surface temperature of the drop, treated as a wet-bulb thermometer. With this correction rdr/dt was found to be proportional to $\{\rho_v(s)-\rho_v\}$ over a certain range, as shown

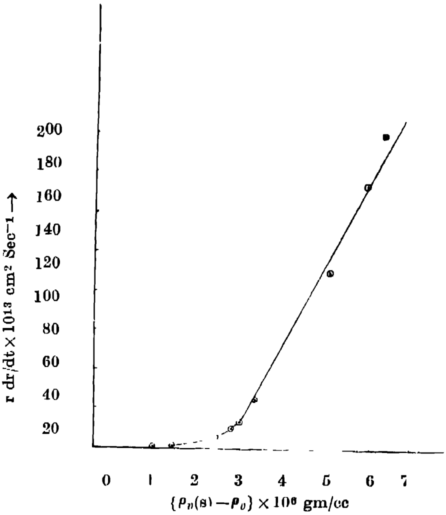

Fig. 3. Variation of $r\frac{dr}{dt}$ with humidity

in Fig. 3. Each point plotted for this graph is a mean value of three to four similar observations. For low values of $\{\rho_v(s)-\rho_v\}$ however, slight departure from this trend, is indicated.

DISCUSSION OF THE RESULTS

Using Maxwell's expression for the evaporation rate given in equation 1, one finds that the value of dr/dt is equal to 3.8×10^{-3} cm sec^{-1} for $r = 1\mu$, $D = 0.26$, the pressure 76 cm of Hg, temperature 28°C and relative humidity 0.85. Using Fuchs expression given in equation 2, with $\alpha = 0.036$ and all other values as indicated above, one obtains $dr/dt = 6.6\times10^{-4}$ cm sec^{-1}. The experimentally observed observed value is 7.0×10^{-9} cm sec^{-1}. Thus, it is obvious that these theoretical values are much too large, as compared to that of the observed ones.

It is extremely important however, to note that the experimentally observed values, agree well with the value obtained by Gudris and Kulikowa (1924). Their value for the above case, is $dr/dt = 6.3\times10^{-9}$ cm sec^{-1}. As already stated, their droplets were freely suspended and charged and the rate was many times less than the theoretical. Thus, it is confirmed that the water droplets of one micron size, evaporate considerably slowly, than that calculated from Fuchs expression. The two possibilities which might help in explaining this descripency are

(1) Both the equations, of Maxwell as well as of Fuchs, have not been tested for very small drops of micron size and shown to be true in this range; and

(2) These equations are derived for drops which are not charged. It is true that the charge has no significant effect for bigger drops of say, 1 mm diameter However, there is some evidence as stated below to suggest that the charge may be effective for very small droplets, in reducing their evaporation rates.

Careful measurements of freely falling water drops, at 0-40°C and 10-100% relative humidity have been made by Kinzer and Gunn (1951), using refined electronic technique. Drops of diameter ranging from 40μ to 1mm were produced and electrified by dropper. Of exceptional interest are the measurements in the region of very small Reynolds numbers. The results of Kinzer and Gunn indicate that very small droplets, whose motions are controlled largely by viscous forces, evaporate relatively slowly.

Thus the problem of the rate of evaporation of charged water droplets of very small size, can by no means be considered as solved.

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